A comparative study for Hydrogen storage in metal decorated graphyne nanotubes and graphyne monolayers

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ABSTRACT

A comparative study for hydrogen storage in metal decorated graphyne nanotubes and graphyne monolayers has been investigated within the framework of first-principle calculations. Our results show that the binding energies of Li, Ca, Sc, Ti on graphyne nanotubes are stronger than that on graphyne monolayers. Such strong binding would prevent the formation of metal clusters on graphyne nanotubes. From the charge transfer and partial density of states, it is found that the curvature effect of nanotubes plays an important role for the strong binding strength of metal on graphyne nanotubes. And the hydrogen storage capacity is 4.82 wt%, 5.08 wt%, 4.88 wt%, 4.76 wt% for Li, Ca, Sc, Ti decorated graphyne nanotubes that promise a potential material for storing hydrogen.

1. Introduction

High gravimetric and volumetric density hydrogen storage materials usually prefer to choose the materials with light mass elements, large surface ratio and multi-pores. Among those materials, carbon based nanomaterial such as carbon nanotube, carbon fiber, fullerene, graphene can be used to store hydrogen. For example, hydrogen molecules could adsorb to pure graphene through physical absorption with the binding energy of 90 meV [1,2]. Using single-walled carbon nanotube bundles and peapods as hydrogen storage materials, hydrogen molecules can squeeze in the inter-tube space at about 350 K [3]. Other carbon based nanomaterials like carbon fibers [4], C_{60} fullerenes [5,6] and graphene-oxide Frameworks [7] are suited to storing hydrogen. Although carbon based nanomaterial with many adsorbed sites for hydrogen to bind, the physical interaction among them is too weak and needs special conditions like low temperature and high pressure to hold the hydrogen molecules. It is easy for hydrogen molecules to get away from pure carbon nanomaterial, resulting in cutting the capacity of storing hydrogen.

It is found that dispersing metal atoms on carbon nanomaterial could enhance the binding strength between hydrogen molecules and substrate materials. It has been demonstrated that Li [8] and Ti [9] decorated graphene could hold four hydrogen molecules per

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metal atom with an idea hydrogen adsorbing energy of -0.20 eV and -0.42 eV, respectively. Adding Al [10] to carbon nanotube could obtain a hydrogen storage capacity of 6.15 wt% with the average hydrogen adsorption energy of -0.214 eV. Previous studies have pointed out that metal atoms, such as Li, Ca, Sc and Ti, which disperse on the surface of single-wall carbon nanotube or C_{60} fullerenes, could be received as promising hydrogen storage materials [11–13]. However, the adsorbed metal atoms prefer to cluster on the surface of substrates, resulting in the reduction of hydrogen storage capacity [14–16]. Different from the carbon nanomaterials which only involve sp^2 hybrid C atoms mention above, graphyne involves sp^2 and sp hybridization. Graphyne has more additional free π-electron that may have a strong interaction to metal atoms. When metal atoms get close to substrate, more electron of metal transfer to the sp hybrid C atoms, resulting in the enhancement of the interaction between them and prevent metal from formation of clusters. It is to bring the hope of using graphyne as hydrogen storage materials. In order to enhance the binding strength of metal, Guo et al. [17] and Zhang et al. [18] had added a Li atom on the surface of γ-graphyne, and found the binding energy of metal is stronger than that on graphene through first principle calculation. However, the binding strength decrease with the number of metal atoms increasing and herein metal atoms could easily form clusters. Graphyne nanotube is an acetylene tube which is curled by γ-graphyne monolayers. And ones can imagine that a stronger interaction between metal and the curving acetylene rings can be obtained due to the curve effect.

Here we contrastively investigated the binding strength of several light metals (Li, Ca, Sc, Ti) on γ-graphyne and graphyne
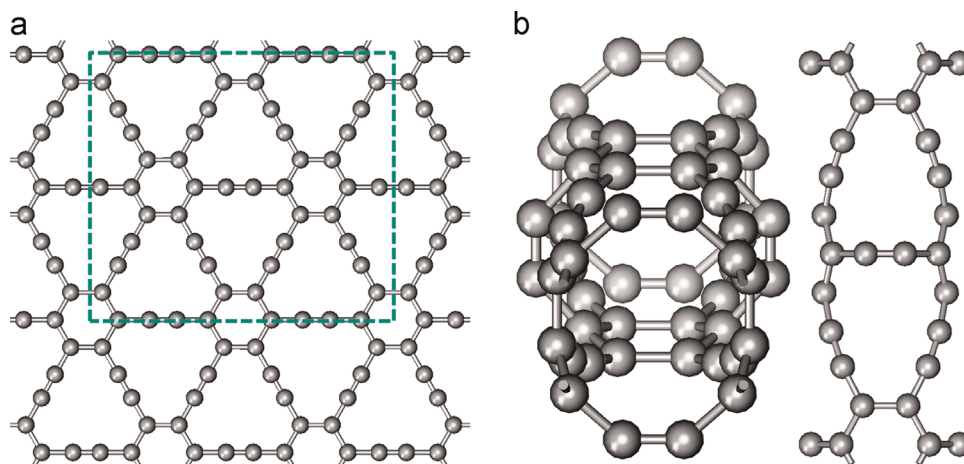
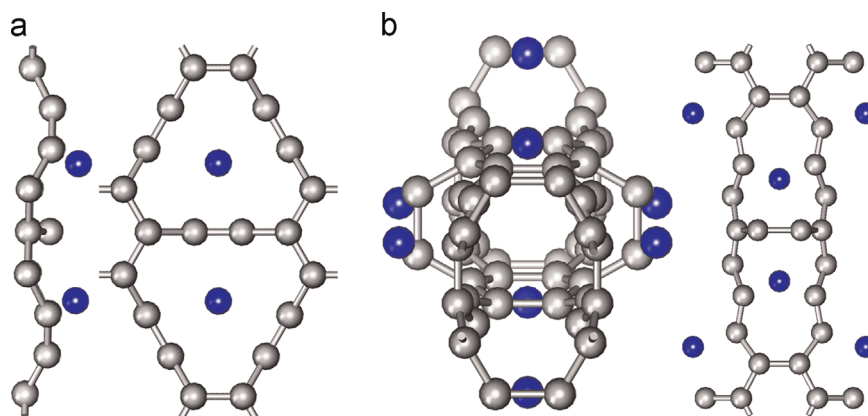**Fig. 1.** The optimized geometry of γ-graphyne monolayer (a) and graphyne nanotube (b).

Fig. 2. The side view and top view for optimized geometry of metal atoms on γ-graphyne monolayer (a) and graphyne nanotube (b).

Table 1

The average binding energy E_b of metal atoms adsorbed on substrate, the Mulliken charge for each metal atom and the distance d_{M-C} between metal and the nearest C atom of substrate.

	γ-graphyne monolayer			graphyne nanotube		
	E_b (eV/M atom)	Mulliken (e/M atom)	d_{M-C} (Å)	E_b (eV/M atom)	Mulliken (e/M atom)	d_{M-C} (Å)
Li	−0.583	0.434	2.243	−0.743	0.466	2.229
Ca	−0.083	0.641	2.808	−0.948	1.387	2.421
Sc	0.861	0.583	2.333	−0.718	0.810	2.184
Ti	1.630	0.611	2.248	−0.431	0.769	2.051

Table 2

E_{ad} is the average adsorption energy for different numbers of hydrogen molecules adsorbed on metal@graphyne nanotube, Capacity is the hydrogen storage capacity of different metals decorated graphyne nanotube.

	$E_{ad}(1H_2)$ (eV)	$E_{ad}(2H_2)$ (eV)	$E_{ad}(3H_2)$ (eV)	Capacity (wt%)
Li	−0.146	−0.093	/	4.82
Ca	−0.208	−0.141	−0.137	5.08
Sc	−0.251	−0.166	−0.206	4.88
Ti	−0.243	−0.215	−0.198	4.76

nanotube through ab initio calculations. We found the interaction between metal to nanotubes is much stronger than that to the graphyne monolayers. The strong interaction would prevent metal atoms from cluster on the surface of graphyne nanotube. The curved acetylene rings are beneficial to hold metal atoms, and

promise an idea hydrogen storage capacity of 5.08 wt% for Ca@-graphyne nanotube.

2. Computational details

Fully relaxed geometry optimizations and total energy for metal decorated graphyne monolayers and graphyne nanotube were carried out by the Vienna ab initio simulation (VASP) [19] with the projector-augmented-wave (PAW) method [20]. The Mulliken charge analysis was implemented in the DMol3 package [21] for counting out the transferred electrons from metal atoms to substrate. The exchange-correlation energy was described by the Perdew–Burke–Ernzerhof function [22] of the generalized gradient approximation (GGA-PBE function), and the cutoff energy was 400 eV. All structural optimizations were obtained by using the Hellmann–Feynman force less than 0.01 eV/Å and a convergence tolerance of energy was 10^{-5} eV. A vacuum space of 20 Å was needed to avoid the interaction between neighboring systems.

3. Results and discussion

As shown in Fig. 1(a), γ-graphyne belongs to the trigonal crystal system with 12 carbon atoms per primitive cell. The lattice constant is 6.896 Å which consists with the previous work [23]. Curling a (2×2) supercell of γ-graphyne (dashed box in Fig. 1(a)), one can obtain a graphyne nanotube with 48 carbon atoms in it. Fig. 1 (b) is the side and top view of graphyne nanotube, and the lattice